



Ammonia removal from secondary effluent by selective ion exchange with clinoptilolite
by David Irvin McCready

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Civil Engineering
Montana State University
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Abstract:

The objective of this study was to provide information necessary for the application of selective ion exchange to large, scale operation in wastewater treatment. The ammonia-nitrogen removal processes are described. The advantages and disadvantages of each process are listed. Low temperature (4°C) and high temperature (33°C) exhaustion may be predicted by Figure 16. The clinoptilolite weight loss after 100 cycles of exhaustion and regeneration ranged from 0.31 to 0.56 percent per cycle for regenerant pH of 11.0 to 12.5. There was 2.3 percent permanent loss of exchange capacity after 100 cycles. Organic fouling temporarily reduced exchange capacity by 11 percent. The least cost of regeneration occurs with the reuse of calcium oxide regenerant. At pH 11.5 the cost is \$0,030/1000 gallons with 0.24 lb NaCl/gallon.

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AMMONIA REMOVAL FROM SECONDARY EFFLUENT
BY SELECTIVE ION EXCHANGE
WITH CLINOPTILOLITE

by

DAVID IRVIN MCCREADY

A thesis submitted in partial fulfillment
of the requirements for the degree


of

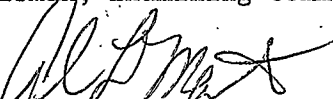
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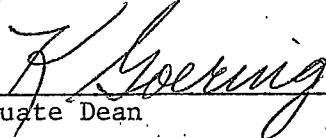
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ABSTRACT

The objective of this study was to provide information necessary for the application of selective ion exchange to large scale operation in wastewater treatment. The ammonia-nitrogen removal processes are described. The advantages and disadvantages of each process are listed. Low temperature (4°C) and high temperature (33°C) exhaustion may be predicted by Figure 16. The clinoptilolite weight loss after 100 cycles of exhaustion and regeneration ranged from 0.31 to 0.56 percent per cycle for regenerant pH of 11.0 to 12.5. There was 2.3 percent permanent loss of exchange capacity after 100 cycles. Organic fouling temporarily reduced exchange capacity by 11 percent. The least cost of regeneration occurs with the reuse of calcium oxide regenerant. At pH 11.5 the cost is \$0.030/1000 gallons with 0.24 lb NaCl/gallon.

CONCLUSIONS

Selective ion exchange has several advantages for the removal of nitrogen from wastewater including: (1) little effect of low temperature on removal efficiency, (2) almost complete removal of ammonia, and (3) favorable economics. The objective of this investigation was to provide information necessary for using clinoptilolite for ammonia removal in large scale operations. The following conclusions were made regarding long term cyclic operation of clinoptilolite ion exchange columns:

(1) The attrition rate for the zone of maximum weight loss (the bottom of the exchange bed for upflow exhaustion) will range from 0.31 to 0.56 percent per cycle for regenerant pH levels of 11.0 to 12.5.

(2) Regeneration at pH 11.5 is the maximum caustic level for minimum attrition, at lower pH levels regeneration is less efficient and the attrition rate does not decrease significantly.

(3) Exposure to 100 cycles of exhaustion with domestic wastewater and regeneration at pH 11.0 and 12.5 resulted in 2.3 percent permanent loss of ammonia exchange capacity.

(4) Organic fouling of clinoptilolite can cause up to 11 percent temporary loss of exchange capacity in cyclic exhaustion with filtered secondary effluent unless proper backwashing prior to regeneration is practiced every cycle.

The effect of feedwater temperature on clinoptilolite column exhaustion is summarized as follows:

(5) Optimum conditions for exhaustion occur at room temperature. Exhaustion at temperatures ranging from 4 to 33°C resulted in 12.5 to 16 percent change of feedwater volume treated and 0.10 to 0.14 mg/l $\text{NH}_3 - \text{N}$ change of ammonia leakage concentrations. Low and high temperature exhaustion performance can be predicted for the given conditions using Figure 16.

The following conclusions were made regarding the cost of clinoptilolite regeneration.

(6) Minimum regeneration cost results with the reuse of calcium oxide regenerant. At pH 11.5 the regeneration cost is \$0.030/1000 gallons.

(7) The cost of sodium chloride, \$0.012/lb, is a large proportion of the regeneration costs both with and without regenerant reuse.

CHAPTER I

INTRODUCTION

Historically, wastewater treatment consisted of removal of settleable solids, biodegradable organics, and bacteria. But the increasing intensity of water reuse coupled with increased public reaction to degradation of aquatic environments has resulted in regulations for the eventual removal of nitrogen, especially ammonia.

Table 1 lists the range of nitrogen concentrations in raw domestic wastewater.

TABLE 1
NITROGEN CONCENTRATIONS IN RAW DOMESTIC WASTEWATER
(AFTER METCALF AND EDDY, 1972 [35])

Nitrogen type	concentration, mg/l as N
organic	8-35
ammonia	12-50
nitrite	> 0
nitrate	> 0

Organic nitrogen, generally in the form of urea, is readily hydrolyzed to ammonia during wastewater treatment [35]. Although there is some nitrogen removal during conventional biological treatment, it is not great enough to have a marked effect on the effluent quality.

Future federal effluent standards will limit the ammonia-nitrogen concentration in treated wastewater either directly by ammonia concentration standards or indirectly by Biochemical Oxygen Demand (BOD)

standards. Reasons to limit the wastewater ammonia-nitrogen concentration are:

(1) Low concentrations of ammonia are toxic to fish and other aquatic life. Concentrations as low as 2.5 mg/l $\text{NH}_3\text{-N}$ may be toxic to salmonids [35].

(2) Ammonia corrodes portland cement concrete and metals such as copper and brass.

(3) Ammonia is a plant nutrient. If it is the growth-limiting substance, ammonia addition will accelerate the eutrophication of lakes and streams.

(4) Ammonia in natural waters is easily oxidized to nitrites and nitrates, thus adding to the oxygen depletion of the receiving water. Oxygen depletion limits the type of aquatic life capable of survival. Less desirable species of fish are associated with low oxygen levels [31].

(5) Nitrate concentrations greater than 60-150 mg/l may cause the disease, methemoglobinemia, which can be fatal to humans and livestock. The 1962 United States Public Health Service standards set 40 mg/l as the allowable nitrate concentration for domestic use.

(6) Ammonia reacts with chlorine during wastewater disinfection increasing the chlorine demand.

Ammonia and oxidized forms of nitrogen in excess restrict the reuse and disposal of wastewater.

Objectives

This study was intended to complement and complete existing knowledge of ammonia removal by selective ion exchange using clinoptilolite. The general objectives were to establish criteria under which the most feasible method of ammonia removal could be chosen and to define more completely the effects of long term selective ion exchange operations. The study had the following specific objectives:

1. To compare methods of ammonia removal in such terms as cost and removal efficiency, and explain briefly each process including inherent advantages and disadvantages.

2. To compile existing knowledge from previous investigations of selective ion exchange with clinoptilolite.

3. To define the effects of long term operation, such as loss of exchange capacity, attrition rate, organic fouling and temperature effects more completely, as would be needed for large scale application of clinoptilolite to ammonia removal.

4. To establish a method of easy computation of the minimum cost of regeneration.

Limitations

- (1) Attrition and organic fouling studies were performed with Bozeman wastewater. Temperature effects were studied with fortified tapwater.

- (2) Two exhaustion runs were made in each temperature range.
- (3) The full exchange capacity was restored to the clinoptilolite every 25 cycles during the attrition studies when the samples were heated to 600°C to destroy organic coatings.
- (4) Only 100 cycles of exhaustion and regeneration were performed in the long term studies.
- (5) All ammonia-nitrogen removal costs are given for a 10 MGD operation.
- (6) The regeneration costs of clinoptilolite were optimized for a 10 MGD operation.
- (7) Several assumptions, necessary for optimization of regenerant cost, are explained in Chapter VII.

Symbols

Symbols and abbreviations are defined in Appendix A.

CHAPTER II

AMMONIA-NITROGEN REMOVAL METHODS

Many processes have been developed for the removal of ammonia and the oxidized forms of nitrogen from wastewater. Selection of a given process or combination of selected processes depends on:

- (1) The use to be made of the treated wastewater, which normally governs the allowable nitrogen content.
- (2) The available means for ultimate disposal of contaminants, such as nitrogen-rich brines from reverse osmosis.
- (3) The process economics.
- (4) The other waste substances removed. Some processes remove only nitrogen, whereas others remove deleterious substances such as phosphorus and salts.

The five principal ammonia-nitrogen removal methods are ammonia stripping, biological nitrification-denitrification, breakpoint chlorination, selective ion exchange, and land disposal. Other methods which have been investigated for nitrogen removal are reverse osmosis, conventional ion exchange, electro-oxidation, electrodialysis, algae harvesting, and distillation. Some of these methods can be combined, such as nitrification-denitrification with breakpoint chlorination as a polishing operation.

All cost estimates for the above processes are based on a 10 MGD operation with a total ammonia-nitrogen concentration of 20 mg/l $\text{NH}_3\text{-N}$.

The cost estimates were updated to an Engineering News Record Construction Cost Index of 2200, estimated to occur in January, 1975 [22].

Ammonia Stripping

The removal of ammonia from wastewater by ammonia stripping involves aeration to remove dissolved ammonia gas. The solution pH must be adjusted to greater than 11.0 prior to being pumped to a stripping tower. The ammonia solution is allowed to fall downward against an upflow of air (or at right angles for a side draft system). Because ammonia release occurs at the instant water droplets are formed, towers are designed for continuous droplet formation and coalescence [18]. The circulation of air maximizes the air-water ammonia concentration differential, thus increasing the removal rate. The release of ammonia can occur only when the ammonia is in the dissolved gaseous form. The high pH is necessary to shift the equilibrium equation (1) to the right.

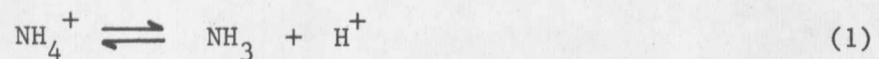


Figure 1 illustrates the relationship between pH, temperature, and the form of ammonia. Most of the ammonia can be maintained in the ammonia form by maintaining a high organic loading rate on the secondary process [21]. The ammonia extracted generally escapes into the atmosphere. The wastewater pH must be lowered from approximately pH 10.5 to 8.0 with acid or other means prior to discharge.

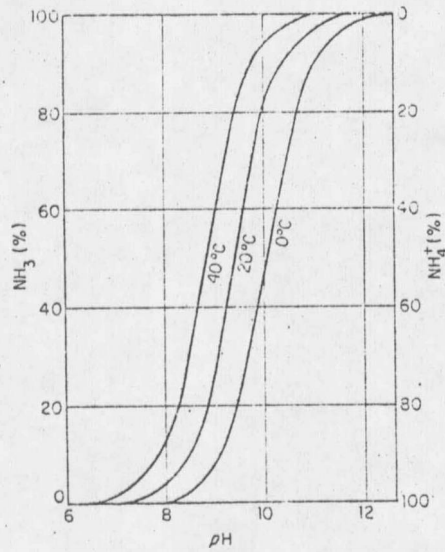


FIGURE 1: THE EFFECTS OF pH AND TEMPERATURE ON THE DISTRIBUTION OF AMMONIA AND AMMONIUM ION IN WATER (AFTER CULP AND CULP, 1971 [18]).

Process advantages. (1) This is an efficient process for high ammonia concentrations (>50 mg/l $\text{NH}_3 - \text{N}$) at high pH (>11.0) and high temperature ($>20^\circ\text{C}$). Ammonia removal efficiency of 98 per cent may occur under optimum conditions [20].

(2) This is the most economical ammonia removal method, \$0.04/1000 gallons, as shown in Figure 2 and Table 2. It requires relatively inexpensive equipment, little control, and lime for pH control is partially recoverable [47].

(3) Some phosphorus removal occurs due to the high pH necessary for the process [20].

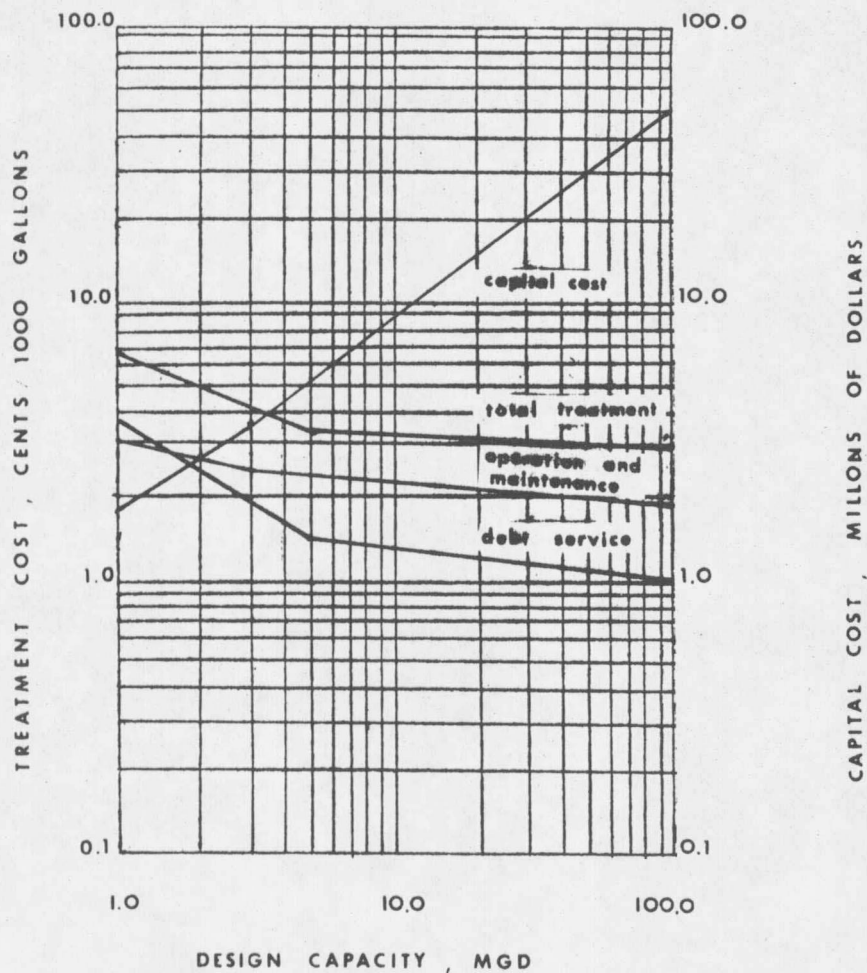
Process disadvantages. (1) The high pH causes carbonate precipitation which may clog the stripping tower. In addition the carbonate scale may be difficult to remove [18].

(2) The process removal efficiency drops to 50-60 per cent for average ammonia concentrations (20 mg/l $\text{NH}_3 - \text{N}$) as air temperature approaches freezing [18].

(3) Ammonia must be in the dissolved gaseous form to be removed.

(4) The release of ammonia into the atmosphere may be undesirable in urban areas and furthermore the extracted ammonia may redissolve in the receiving water due to its high solubility.

(5) It is difficult to achieve low effluent ammonia concentrations, at best 10% or 2-5 mg/l $\text{NH}_3 - \text{N}$ remain in the effluent. Approx-



ENR = 2200 , EST. DATE : JAN., 1975

FIGURE 2: AMMONIA STRIPPING. CAPITAL COST, OPERATION AND MAINTENANCE, DEBT SERVICE VS DESIGN CAPACITY (AFTER SMITH,1968 [47]).

TABLE 2

COMPARISON OF NITROGEN REMOVAL PROCESSES

Process	Removal Efficiency, %	Cost Estimate, \$/1000 gal ^a	References	Remarks
Conventional Air Stripping	50-98	0.04-.06	18	Costs for summer operation
Modified Air Stripping (ARRP)	85+	0.06-.12	28	Preliminary cost estimate
Nitrification-Denitrification	50-90	0.12-.13	16,18,36,43	
Conventional Ion Exchange	80-90	0.60-.70	18,36	Excluding costs of pretreatment and brine disposal
Selective Ion Exchange	85-98	0.12-.18	29	Excluding costs of pretreatment and brine disposal
Breakpoint Chlorination	100	0.09-.10	18,37,42	May require carbon adsorption
Breakpoint Chlorination With Carbon Adsorption	100	0.25-.26	18,37,42	
Land Disposal By Spray Irrigation	0-91	0.13-.26	21,36,48	Cost dependent on location
Algae Harvesting	40-60	0.04-.06	21,16	Excluding cost of algae disposal, cost dependent on location

TABLE 2 (CONTINUED)

Process	Removal Efficiency, %	Cost Estimate, ^a \$/1000 gal	References	Remarks
Reverse Osmosis	32-92	0.45-.50	1,18,36	Excluding costs of pretreatment and brine disposal
Electrodialysis	40+	0.27-.30	2,47	Excluding cost of pretreatment and brine disposal
Electro-oxidation	70-95	0.70-.75	27	
Distillation	0-100	0.69-1.73	21	Nitrous acid may escape with the distillate

^aCost estimates are based on a 10 MGD operation with an initial 20 mg/l NH₃-N concentration. Engineering News Record Construction Index = 2200, estimated date January, 1975.

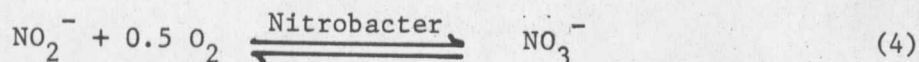
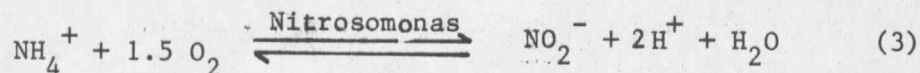
imately 5-6% of this nitrogen is not in the removable form [18].

A modified ammonia stripping system (Ammonia Removal and Recovery Process) has been developed by CH₂M Engineers of Redding, California. This process eliminates the problems of carbonate precipitation, reduced efficiency at low temperature, and the escape of ammonia into the atmosphere. This process utilizes a closed air circulation system, so no carbonate precipitation can occur after the initial carbon dioxide in the system precipitates. This system can maintain high removal efficiency by exclusion of cold outside air. The ammonia is concentrated in an aqueous solution maintained at below pH 6.0 with sulfuric acid. Although the process cost is 1.5 to 2.0 times the cost of conventional stripping, costs may be reduced by the sale of ammonia for liquid fertilizer. Further process design optimization is planned by use of a pilot facility operating on lime clarified secondary effluent [28].

Biological Nitrification-Denitrification

This process consists of microbiologically oxidizing all the ammonia in wastewater to nitrates (nitrification) and then microbiologically reducing the nitrates to nitrogen gas (denitrification) which is released to the atmosphere. A three stage biological system is generally used although the process is adaptable to a two stage system. The first stage, which removes most of the carbonaceous BOD, can be an activated sludge or trickling filter process. The second and third stages are nitrification and denitrification units, respectively.

Nitrification can occur in two steps as represented in equations (3) and (4).

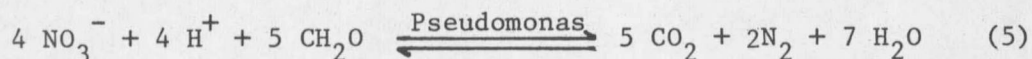


Chemosynthetic autotrophic bacteria, such as Nitrosomonas, Nitrosococcus, Nitrosospira, Nitrocystis, and Nitrosogloes, obtain energy for cell synthesis from the oxidation of ammonia to nitrites. The nitrites then serve as an energy source for other chemosynthetic autotrophic bacteria such as Nitrobacter during nitrite oxidation to nitrate [43].

Nitrification must be complete to assure complete denitrification. The basic conditions for nitrification are: (1) at least 0.5 mg/l dissolved oxygen, (2) cell detention time in the reactor of at least 8 hours, and (3) a low reactor loading rate (<0.3 lb BOD/lb mixed liquor suspended solids-day) [18]. Nitrification rate decreases with decreasing water temperature. The reactor volume required at 10°C would be three times that required at 20°C for a complete-mix system [35].

Denitrification is an anaerobic process which occurs when facultative anaerobic bacteria, such as Pseudomonas, Achromobacter, Bacillus, and Micrococcus use nitrate instead of oxygen as a hydrogen ion acceptor

in the electron transport system [40]. Denitrification may be represented by equation (5).



During the process, nitrates are reduced to nitrogen gas and carbon compounds are oxidized.

The basic requirements for denitrification are: (1) an organic carbon source, (2) a dissolved oxygen concentration of less than 0.5 mg/l, and (3) a pH of approximately 6.5 [16]. The process proceeds too slowly to be practical when utilizing the carbon remaining after secondary treatment, hence the addition of a biodegradable carbon source is necessary. Raw sewage has been added as a carbon source, but this has the limitation of adding unoxidized nitrogen compounds and additional BOD to the final effluent. Methanol is the least expensive carbon source at the present time.

The denitrification rate is also temperature dependent. Denitrification can occur in three possible designs: anaerobic activated sludge, anaerobic filter, and anaerobic lagoon. An optimum removal efficiency of 90 per cent is possible with the nitrification-denitrification system.

Process advantages. (1) Ammonia and the oxidized forms of nitrogen are removed by this process.

(2) The conversion of wastewater nitrogen compounds into free nitrogen does not pollute the environment.

(3) The costs and removal efficiency of this process are competitive with other removal processes, as shown in Figure 3 [36].

(4) The structures required are of simple design.

(5) This system can be used to either produce a nitrified effluent or to remove nitrogen compounds. Thus the process can be constructed in steps to meet standards of the present and the future as they are required.

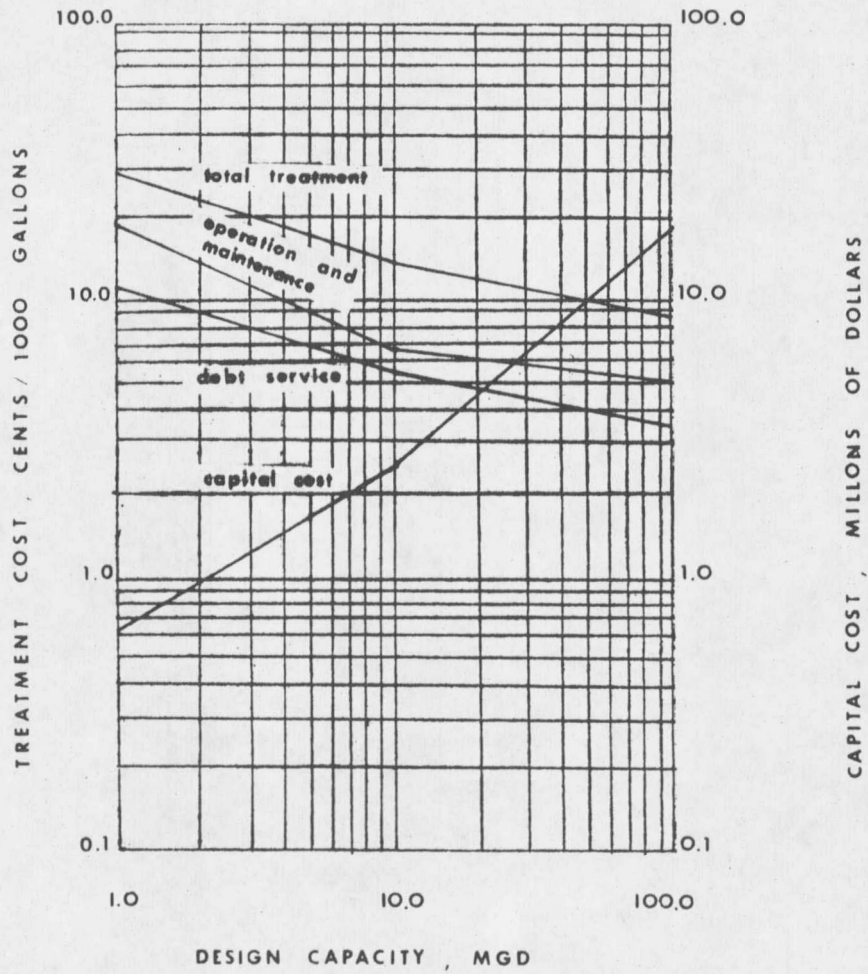
Process disadvantages. (1) Nitrification and denitrification rates are reduced significantly by low wastewater temperatures.

(2) The process will be difficult to control. Process failure may occur due to cell washout, short circuiting, inhibiting substances, or failure to maintain anaerobic conditions in the denitrification unit.

(3) The process must operate continuously to maintain microbial populations.

(4) An exceptionally knowledgeable operator is required to run the process.

(5) At optimum removal efficiency, 2-5 mg/l nitrogen remains in the final effluent. A polishing operation such as breakpoint chlorination may be required.



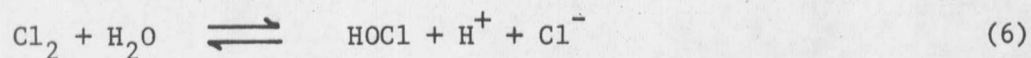
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FIGURE 3: BIOLOGICAL NITRIFICATION AND DENITRIFICATION. CAPITAL COST, OPERATION AND MAINTENANCE, DEBT SERVICE VS DESIGN CAPACITY (AFTER MONTI AND SILBERMAN, 1974 [36]).

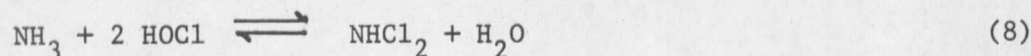
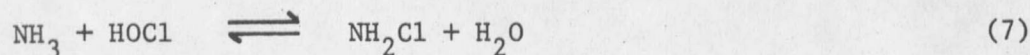
Breakpoint Chlorination

Breakpoint chlorination consists of using chlorine to oxidize ammonia to nitrogen gas and to reduce nitrates and nitrites to nitrogen gas. This process has been used extensively for the disinfection of water and wastewater, however its use to remove nitrogen from wastewater is a recent innovation.

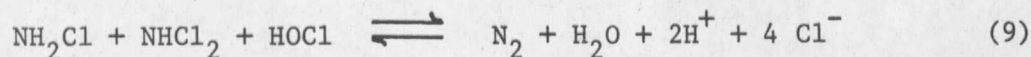
The addition of chlorine to water forms hypochlorous acid as shown in equation (6).



The reaction of hypochlorous acid with ammonia to form monochloramine and dichloramine is shown in equations (7) and (8), respectively.

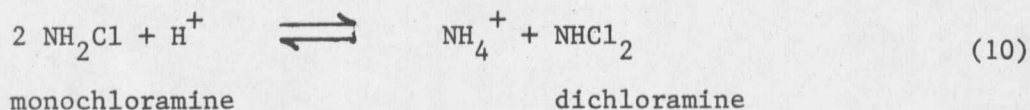


The reaction of monochloramine and dichloramine with hypochlorous acid to produce nitrogen gas is shown in equation (9) [35].



With mole ratios of chlorine to ammonia up to 1:1, both monochloramine

and dichloramine are formed. The relative amounts of each are a function of the pH. Large proportions of dichloramine appear at lower pH in accordance with the equilibrium equation (10).



Further increases in the mole ratio of chlorine to ammonia result in formation of dichloramine, as shown in equation (8), or the production of nitrogen gas as shown in equation (9). These reactions are essentially complete when two moles of chlorine have been added for each mole of ammonia originally present. Chloramine residuals usually reach a maximum when one mole of chlorine has been added for each mole of ammonia and then decline to a minimum at the chlorine -to- ammonia ratio of 2:1. Further additions of chlorine produce free chlorine residuals as shown in Figure 4. Chlorination of water to the extent that all the ammonia is converted to oxidized free nitrogen or other gases is referred to as "breakpoint chlorination" because of the peculiar character of the chlorine residual curve, as shown in Figure 4. It is generally assumed that 10 milligrams of chlorine are required per milligram of ammonia to reach the breakpoint. Nitrous oxide and nitrogen trichloride have been identified among the gaseous products of the breakpoint reaction [42]. Essentially all the ammonia can be oxidized to nitrogen gas and the production of other undesir-

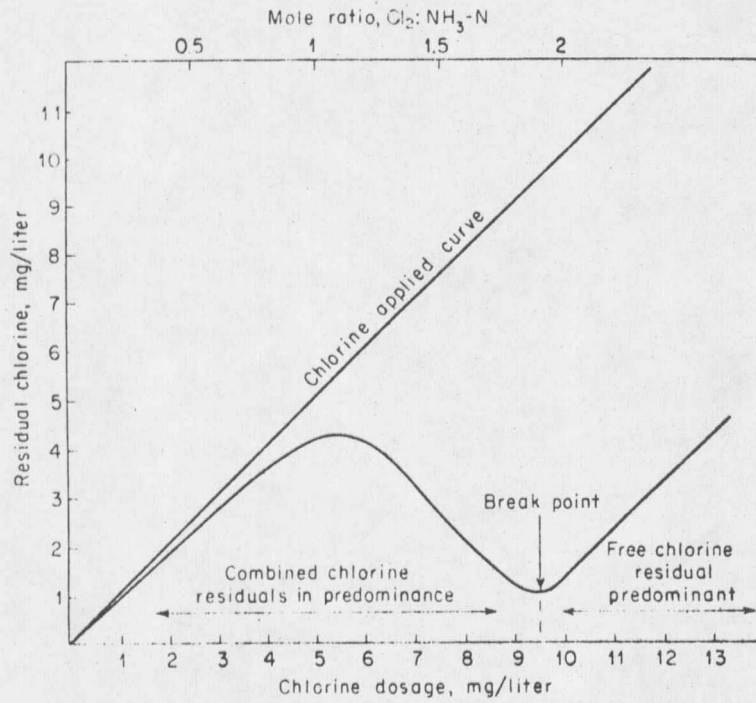


FIGURE 4: A RESIDUAL CHLORINE CURVE SHOWING A TYPICAL BREAKPOINT. THE AMMONIA NITROGEN CONTENT OF THE WATER IS 1.0 MG/L (AFTER SAWYER AND MCCARTY, 1967 [42]).

able products can be eliminated by pH control [14]. The hydrochloric acid formed during chlorination will react with the alkalinity of the wastewater and the pH drop will be slight [35].

Process advantages. (1) Chlorine dosage and pH are the only control necessary.

(2) Production of nitrogen gas is not ecologically undesirable.

(3) This process can achieve almost 100 per cent ammonia-nitrogen removal.

Process disadvantages. (1) The presence of organics, iron (II), or manganese (II) increases the chlorine demand.

(2) Carbon adsorption is necessary to remove chloramines not destroyed by chlorination.

(3) This process increases the chlorides in the effluent 200-500 mg/l. This may restrict the reuse or disposal of the final effluent.

(4) The cost of breakpoint chlorination (\$0.092/1000 gallons), as shown in Table 3, is comparable to other removal methods. However the addition of carbon adsorption (\$0.16/1000 gallons) as shown in Figure 5, increases the cost beyond economic feasibility for removal of the major portion of ammonia nitrogen concentrations [36]. Breakpoint chlorination could be used economically to remove 2-5 mg/l ammonia-nitrogen remaining after less efficient but more economical

TABLE 3

CAPITAL AND OPERATING COSTS FOR BREAKPOINT CHLORINATION^a
 (AFTER PATTERSON AND BANKER, 1971 [37])

Item	Value
Total Capital Costs, dollars	
Chlorination equipment, chlorine feed building, chlorine storage building, contact basin, earthwork, and baffles	532,000
Amortized Cost ^b , dollars	49,500
Capital Cost, dollars/1000 gal	0.014
Operating Costs, dollars/year	
Chlorine	180,000
Materials	4,500
Maintenance and labor	<u>100,000</u>
Total Operating Costs, dollars/year	284,500
Operating Cost, dollars/1000 gal	0.078
Total Cost, dollars/1000 gal	0.092

^a10 MGD system with 20 mg/l NH₃-N; Engineering News Record Construction Cost Index of 2200, estimated January, 1975.

^b15 year life at 7% interest rate.

